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Short Communication

Dielectric Loss of *N*-Substituted Nylon 6.6 and of Polyester 6.6

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In this report the results are summarized of measurements concerning the influence of intermolecular hydrogen bridge formation on the mechanisms responsible for the so-called β- and γ-relaxations in the dielectric loss spectrum of nylon 6.6*) (see McCrum et al.[1], p. 478–497). To that end the loss spectra and the IR carbonyl absorptions in the range from 1500 to 1700 cm^{-1} were studied of polyester 6.6**) and of nylon 6.6, modified by partly substitution of amide-hydrogen by methyl or ethyl groups. This work is intended to give a contribution to the elucidation of the still existing controversy[2–5] concerning the mechanisms mentioned above. Up till now, the idea of *Woodward* et al.[6] of *N*-substitution as a tool in the interpretation of these secondary transitions in the dielectric loss spectrum of nylon 6.6, was not pursued further.

The polyamides were prepared by the (co)polymerization of two types of salt ((I) and (II)). Salt (I) was prepared from adipic acid (used as received; Fluka, purum) and hexamethylenediamine (dist.), according to the method of *Beck* and *Magat*[7]. Salt (II) was prepared in the same way from adipic acid and *N*,*N*′-dimethylhexamethylenediamine or *N*,*N*′-diethylhexamethylenediamine. These type (II) salts, however, precipitated slowly from the reaction mixture. They were purified by dissolution in cold ethanol

*) Poly(iminohexamethyleneiminoadipoyl).
**) Poly(oxyhexamethyleneoxyadipoyl).

and precipitation by diethyl ether. The 'methylated' and 'ethylated' salts had melting points of 127 °C and 122 °C, respectively.

The polyamides were prepared by heating (I) or (II), or a mixture of (I) and (II), in a closed system[8] (this is a modification of the original procedure[7]) for one hour at 210 °C, then for one hour at 250 °C and, subsequently, for another hour at 270 °C. The 'degree of substitution' is now defined as the mole ratio of salt (II) to the total amount of salt ((I)+(II)). In order to check, whether this theoretical value was obtained in reality, chemical analyses were performed. The determined ratios of carbon content to nitrogen content (a reliable measure for the degree of substitution, and independent of moisture content) agreed within 2% with the calculated C/N ratios. The polyamides had inherent viscosities (0,5% solution in formic acid) in the range of 0,1 to 0,4 dl/g.

Polyester 6.6 was synthesized according to a well known method[9]. It had an intrinsic viscosity of 0,79 dl/g (at 25 °C in $CHCl_3$) and a number average molecular weight, $\overline{M}_n$, of 28000 (osmometry, toluene, 30 °C).

Dielectric measurements were carried out at frequencies in the range from 200 to 300 kHz on a Schering bridge (Rohde & Schwarz; SRM, UBM, VKB). Graphs of the loss factor $\mathrm{tg}\,\delta$ against temp. as well as against frequency showed secondary (β- and γ-) maxima at nearly the same temps. (within 4 °C) or frequencies (within 20 Hz) as did graphs of the complex part of the dielectric constant ε'' against these variables. The capacity of the measurement cell, equipped with a polyamide containing disc (s. below) was in the range from 100 to 600 pF. The cell plus the sample disc were placed in a chamber, thermostated (by means of a stream of dry N_2) in the range from 50 to −120 °C within ±0,5 °C.

Dried samples of nylon 6.6 or polyester 6.6 were pressed to a thin film. As only small amounts of *N*-substituted polyamides were available, the hard samples (degree of substitution <60%) were powdered and dispersed in polyethylene, while the soft samples were spread between sheets of polyethylene. From these films, discs were cut (diameter: ca. 80 mm, thickness: ca. 0,7 mm) which were always dried (e.g. by heating them for one day i. vac. at 80 °C, or by placing them in a dessiccator over P_2O_5 for at least one month) before mounting them into the cell.

IR spectra were taken of samples dispersed in KBr. The carbonyl absorptions in the frequency range mentioned above are known to shift remarkably when the polarity of the carbonyl group is altered[10,11]. Therefore, considering the behaviour of the carbonyl band in this range, we found peaks at 1635 cm^{-1} for nylon 6.6 as well as for its 100% substituted samples, but at 1725 cm^{-1} for polyester 6.6. From this, we conclude that the polyester carbonyl group is less polar than the nylon carbonyl group, and, as a consequence, that the ester group is probably less polar than the (substituted or unsubstituted) amide group.

Typical dielectric loss spectra are given in Fig. 1. We ascribed the maximum in $\mathrm{tg}\,\delta$ at −45 °C for polyester 6.6 to a glass-rubber (i.e. α) transition, as

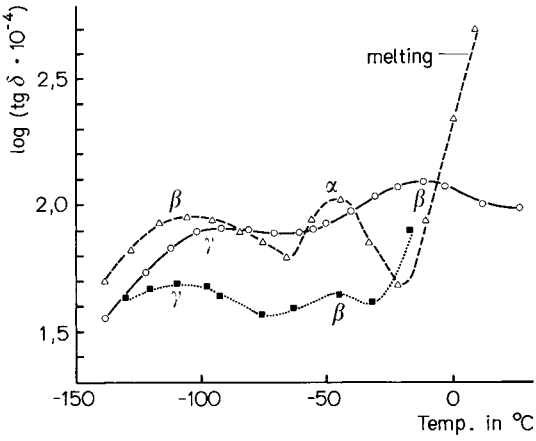

Fig. 1. Dielectric loss spectra of nylon 6.6 (not dispersed in polyethene) (—○—), of polyester 6.6 (not dispersed in polyethene) (– – –△– – –), of 100% *N*-methyl-substituted nylon 6.6 (····■····); frequency in all cases: 200 Hz; tg δ = loss factor

the location of this maximum on the temperature scale turned out to be virtually independent of frequency, thus indicating a high 'activation energy', which is characteristic for this type of transition (s. ref.[1], p. 505). The dielectric β-peak of polyester 6.6 is located in the same temperature region as that of poly(methyleneterephthalate)s (s. ref.[1]), p. 517–520). This transition can be ascribed to complicated, hindered motions of the ester group (together with the methylene sequences) and, perhaps low molecular weight compounds (like H_2O) adsorbed to them. Comparable mechanisms—hindered motions of the amide groups—are proposed for the γ-transition of nylon 6.6 (s. ref.[1], p. 496–497; and refs.[2-5]). That is the reason why polyester 6.6 was involved in our study.

In the loss spectra of nylon 6.6 and *N*-substituted nylon 6.6, in all cases a β-peak was found as a separate peak or as a shoulder on the γ-peak. In duplicate measurements, however, the γ-peak sometimes was present only as a shoulder on the β-peak (without, however, an appreciable change (< 5 °C) in the location of the temperature of the maximum tg δ). These phenomena may be due to incomplete drying or to water absorption (when the sample disc is placed in the cell).

It is seen from the 'activation energy diagram' (Fig. 2) that the results for nylon 6.6, dispersed in polyethylene, do not differ appreciably from those for pure nylon 6.6, giving confidence in our method of dispersing or spreading our *N*-substituted samples in or between polyethylene. Furthermore, it is

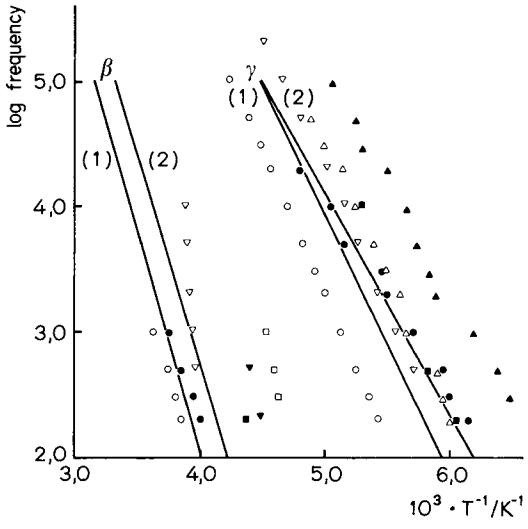

Fig. 2. β- and γ-transition of nylon 6.6 and *N*-substituted nylon 6.6; log frequency (of maximum of tg δ (loss factor)) plotted vs. reciprocal temp. (of maximum of tg δ). Drawn lines: taken from literature ((1): ref.[1], (2): ref.[2]). Points: our measurements. (○): Nylon 6.6 (not dispersed in polyethylene); (●): nylon 6.6 (dispersed in polyethylene); (▲, △): β-transition of polyester 6.6 (not dispersed in polyethylene), duplicate measurements; (▽): 40% *N*-ethyl-substituted nylon 6.6; (▼): 80% *N*-methyl-substituted nylon 6.6; (□): 100% *N*-ethyl-substituted nylon 6.6; (■): 100% *N*-methyl-substituted nylon 6.6

seen from Fig. 2 that the β-transition of polyester 6.6 takes place at a lower temperature than the γ-transition of nylon 6.6, that *N*-substituted has no distinguishable influence upon the temperature of the γ-transition of nylon 6.6, and that *N*-substitution shifts the β-transition of nylon 6.6 significantly towards lower temperature (this shift, however, does not depend distinguishably on the kind of 'substituent'). This last mentioned finding on the behaviour of the β-peak differs from that, formulated by *Woodward* et al.

As to the phenomena, concerning the β- and the γ-transitions of nylon 6.6, we propose an interpretation, based upon the assumptions (a) that a higher transition temperature is caused by a lower mobility of the groups involved, and (b) that this lower mobility is caused either by a higher intermolecular interaction or by the bulkiness of the moving groups. Thus, the same, or almost the same, temperature of the γ-transition of both nylon 6.6 and *N*-substituted nylon 6.6 might mean, that the bulkiness of the —NR—CO-groups has nearly the same effect on the mobility of the groups involved in the transition, as has the intermolecular interaction caused by hydrogen bonding (between —NH—CO-groups of neighbouring chains). Furthermore, the polarity of the (un)substituted amido groups might cause an additional

intermolecular interaction. For the same reasons, the γ-transition temperature of nylon 6.6 and of *N*-substituted nylon 6.6 is higher than the β-transition temperature of polyester 6.6, where the interchain interaction is not strengthened by hydrogen bridge formation and where, possibly, weaker dipoles are responsible for less interaction than in the *N*-substituted nylon 6.6.

Our results show also, that hydrogen bridge formation between neighbouring chains might be an essential factor in the mechanisms, responsible for the β-peak in nylon 6.6. In our opinion, this transition cannot be attributed to motions of polymer-water complex units alone, as propose e.g. *Tuynman*[2] and *Kapur* et al.[3]. Our results, however, are not in disagreement with their conclusion concerning the rôle of polymer-water complex units in the mechanism of the β-transition of nylon 6.6.

For completeness, we mention to have found a shift towards lower temperatures for the α-transition of *N*-substituted nylon 6.6 at increasing degree of substitution.

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